

FABRICATION OF ARRAY PH SENSITIVE EGFET AND ITS READOUT CIRCUIT

BACKGROUND OF THE INVENTION

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1. Field of the invention

This invention relates to a method for fabricating an array pH sensor and a readout circuit of such array pH sensor, and more particularly to a method for fabricating an array pH sensor and a readout circuit of such array pH sensor by
10 utilizing an extended gate ion sensitive field effect transistor (EGFET). The structure of this EGFET in combination with fabrication of biosensors and its readout circuit are produced as an integrated biosensor system. Therefore, the present invention can be applied to some applications such as medical detection, circuit design, semiconductor component fabrication, etc.

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2. Description of the prior art

Conventional glass electrodes have many advantages such as high linearity, excellent ion selectivity and good stability. However, due to the relatively large volume, high cost and long reaction time, the technologies for fabricating these
20 ion selective glass electrodes have been developed toward the technologies of established silicon semiconductor integrated circuits so as to fabricate field effect sensors. Thus, the conventional glass electrodes are replaced.

In 1970, Piet Bergveld [1] has firstly removed the metal portion from the gate electrode of a general metal oxide semiconductor field effect transistor
25 (MOSFET). Then, the device is dipped into an aqueous solution. With the

oxide layer of the sensor's gate electrode serving as an insulating ion sensing membrane, when the transistor is in contact with solutions with different pH values, different potential changes will occur at an interface between the transistor and the solution, such that the current passing through its channel is changed accordingly. In such manner, the pH values or concentrations of other ions can be measured. Thus, this device is referred by Piet Bergveld as a field effect ion sensor .

In 1970's, the studies and the applications of the field effect ion sensors were still under exploration [2]. However, in 1980's, the studies of the field effect ion sensors were promoted to a new level. The studies about those basic principle researches, crucial technologies or practical applications have been greatly progressed [2]. For example, based on the structure of the ion sensitive field effect transistor, the types of field effect transistor fabricated for measuring a variety of ions and chemical substances had more than 20 or 30. In the aspects of miniaturization, module or multifunction, the component has been greatly developed [2-5]. The ion sensitive field effect transistor have been dominated all over the world with several decades of development, because they have the following special features, when compared with the conventional ion selective electrodes [2]:

1. They can be miniaturized to perform microanalysis of solutions.
2. They have high input impedance but low output resistivity.

Due to the above advantages, many research institutes have been interested in researching the ion sensitive field effect transistor since the past twenty years. Some important researches associated such sensors can be depicted as follows:

- (1) miniaturization of reference electrodes [6];

(2) differential field effect ion sensors [7];

(3) field effect ion sensors having immobile enzyme for detecting function information of organisms, for example glucose concentration, oxygen content in blood, etc. [8];

5 (4) exploration of theories, for example adsorptive bonding models;

(5) researches on packaging materials [9];

(6) integration of measurement systems and sensors [10]; and

(7) researches on simulation of field effect ion sensors[11].

The extended gate ion sensitive field effect transistor (EGFET) is one of an
10 ion sensitive field effect transistor and firstly introduced by J. Spiegel [12]. In contrast to the traditional ion sensitive field effect transistor, the extended gate field effect transistor retains the original metal gate of the metal-insulation layer-semiconductor transistor and the sensitive membrane is deposited on the other end extended from the metal gate. Comparing with the traditional ion sensitive field
15 effect transistor, the extended gate ion sensitive field effect transistor has a lot of advantages, for example (1) the conducting line provides electrostatic protection for the sensor; (2) the transistor of the sensor can prevent direct contact with the aqueous solution; and (3) the influence of light on the sensor is reduced.

The first publication associated to the EGFET is disclosed in 1983 [12].
20 However, the papers published on the international journals are insufficient. After 1986, few researchers published the papers associated to EGFET. Until 1988, our research group proposed an improved EGFET structure [13-14], which is divided into two portions, i.e. a sensing portion of $\text{SnO}_2/\text{Al}/\text{SiO}_2$ and a readout circuit portion.

25 The patents related to the ISFET are listed hereinafter.

- (1) U.S. Patent Publication No. 5,833,824, inventor: Barry W. Benton, date of patent: 11/10/1998, entitled "Dorsal substrate guarded ISFET sensor" disclosed an ion sensitive field effect transistor (ISFET) sensor for sensing ion activity of a solution, wherein the sensor includes a substrate and an ion sensitive field effect transistor. The substrate has front surface exposed to the solution, a back surface opposite to the front surface and aperture extending between the front and back surfaces. This patent connects the back surface of the substrate to the front-end sensor through the aperture surface such that only the back surface region is exposed to the solution.
- (2) U.S. Patent Publication No. 6,353,323, inventor: Fuggle; Graham Anthony, Date of patent: 3/5/2002, entitled "Ion concentration and pH measurement" discloses an apparatus and a measuring method for processing the front-end sensor. The front-end ion sensor comprises an ion selective electrode, a reference electrode and an ion sensitive field effect transistor, all of which are immersed in the solution. The sensor is connected to the pre-amplifier, and the reference electrode is connected to the readout circuit so as to separate the sensor from the reference electrode. Accordingly, plural sensor can use a common reference electrode.
- (3) U.S. Patent Publication No. 5,350,701, inventor: Jaffrezic-Renault; Nicole; Chovelon; Jean-Marc; Perrot; Hubert; Le Perchec; Pierre; Chevalier; Yves, Date of patent: 9/27/1999, entitled "Process for producing a surface gate of an integrated electro-chemical sensor, consisting of a field-effect transistor sensitive to alkaline-earth species and sensor obtained" discloses an improved production process for treating a surface gate comprising a selective membrane as an integrated chemical sensor. A layer of chemically synthesized phosphonate-

based is deposited on the gate region of the field-effect ion sensor, and thus the sensing membrane is reactive to alkaline-earth species. This sensor is effective as a detector for measuring concentration of alkaline-earth species, in particular the calcium ion.

5 (4) U.S. Patent Publication No. 5,319,226, inventor: Sohn; Byung K.; Kwon; Dae H., Date of patent: 6/7/1994, entitled "Method of fabricating an ion sensitive field effect transistor with a Ta₂O₅ hydrogen ion sensing membrane" discloses a radio frequency sputtering method for depositing a tantalum oxide film onto a non-conducting silicon nitride film, i.e. onto the gate region of the ion
10 sensor, thereby forming a field-effect ion sensor having the tantalum oxide/silicon nitride/silicon dioxide. The Ta₂O₅ film has a thickness of from 40x10⁻⁹ to 50x 10⁻⁹ m. Then, the resultant film is annealed at an elevated temperature of 375 °C to 450 °C in oxygen gas ambience for about one hour.

(5) U.S. Patent Publication No. 4,657,658, inventor: Sibbald; Alastair, Date
15 of patent: 4/14/1987, entitled "Semiconductor devices" uses a semiconductor integrated circuit for sensing a physico-chemical property of an ambient. The circuit includes a pair of semiconductor devices having a similar geometric and physical structure. Its readout circuits are connected to the same circuit, and the overall structure thereof comprises a metal oxide semiconductor field effect
20 transistor and a field-effect ion sensor so as to construct a differential module system.

(6) U.S. Patent Publication No. 5,922,183, inventor: Rauh; R. David, Date
of patent: 7/13/1999, entitled "Metal oxide matrix biosensors" uses a metal oxide-
based film as substrate of biological molecules. Such configuration is suitable
25 for developing electrochemical biosensors. The most common metal oxide-

based film is a hydrous metal oxide, which can be conductive or semiconductor and have excellent stability against dissolution or irreversible reaction in aqueous and non-aqueous solutions. The metal oxide can be used for both amperometric and potentiometric sensing of enzymes, antibodies, antigens, DNA strands, etc. Iridium oxide is the preferred embodiment of metal oxide film due to the best sensing feature. Furthermore, some other metals, for example Ru, Ti, Pd, Pt, Zr, etc., have similar features and their oxides are very stable against oxidation damage.

The hydrogen ion sensing membrane commonly used on the gate oxide of the field-effect ion sensitive transistor can be selected from silicon dioxide, silicon nitride, tantalum oxide, aluminum oxide, etc., for example. A field-effect ion sensitive transistor with having a hydrogen ion sensing membrane made of tin dioxide is first fabricated in the laboratory [15]. The characteristics of this field-effect ion sensitive transistor has an approximate Nernst response in a range of from 56 to 58mV/pH, a high linear sensitivity, a long-termed stability with low drift, and a low response time of < 0.1 second. In addition, the temperature of this sensor can be reduced to zero at an appropriate working current.

Since the ion sensitive field-effect transistor can be used to fabricate array ion sensor array pH sensor by means of the semiconductor fabrication process, the sampling number for detection of the sensor will be increased. The error resulting from one single sensing device can be decreased due to the larger sampling number signals. Thus, when the array sensor is used to measure hydrogen concentration in a human body, the result has a high accuracy and a low error so as to enhance its measuring performance. Furthermore, since the ion sensitive field-effect transistor can be miniaturized, the amount of body fluid to be

draw out will be minimized for microanalysis. Due to the rapid reaction time of the ion sensitive field-effect transistor, the array sensor can instantaneously monitor the solution to be measured, thereby reducing measuring time of the tested sample.

5 Accordingly, the above-described prior art product is not a perfect design and has still many disadvantages to be solved.

In views of the above-described disadvantages resulted from the prior art, the applicant keeps on carving unflaggingly to develop method for fabricating an array pH sensor and a readout circuit device of such array pH sensor according to
10 the present invention through wholehearted experience and research.

SUMMARY OF THE INVENTION

An object of the invention is to provide a method for fabricating an array
15 pH sensor and a readout circuit of such array pH sensor, wherein this fabrication method has a lot of advantages such as simple fabrication equipment, cost effectiveness, mass production, etc. so as to be suitable for fabricating disposable sensors. Therefore, in the field of the array pH sensor, the present invention is highly feasible and applicable.

20 The method for fabricating an array pH sensor and a readout circuit device of such array pH sensor that can accomplish the above-mentioned objects are implemented by utilizing an extended gate ion sensitive field effect transistor to construct the array pH sensor and related readout circuit. Thus, the present invention is intended to provide an array sensor structure, i.e. a tin
25 dioxide/metal/silicon dioxide multi-layer structure sensor and a tin dioxide/indium

tin oxide/glass multi-layer structure sensor, by utilizing such method and device.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The drawings disclose an illustrative embodiment of the present invention which serves to exemplify the various advantages and objects hereof, and are as follows:

Fig.1 is the cross-sectional view showing a sensing configuration of $\text{SnO}_2/\text{Al}/\text{SiO}_2/\text{Si}$;

10 Fig. 2 is the cross-sectional view showing the sensing configuration of $\text{SnO}_2/\text{ITO}/\text{glass}$;

Fig. 3 is a flowchart for fabricating the array pH sensor of the present invention;

Fig. 4 is a schematic view showing the Al layer mask;

15 Fig. 5 is a schematic view showing the sensing membrane SnO_2 layer mask;

Fig. 6 is the configuration of the array pH sensor of the present invention;

Fig. 7 is the circuit configuration of the pre-amplifier for the array pH sensor;

Fig. 8 shows the output/input ratio of the pre-amplifier;

Fig. 9 shows the circuit configuration of the switch of the control portion;

20 Fig. 10 shows the circuit configuration of a 2 to 4 decoder of the control portion;

Fig. 11 is a schematic diagram showing the output/input ratio of the circuit combined the pre-amplifier and the control circuit;

25 Fig. 12 is a schematic diagram showing the output/input ratio of the circuit of the array pH sensor;

Fig. 13 is a schematic diagram showing the readout signal of the array pH sensor;

Fig. 14 is a schematic correction curve of the readout signal of the array pH sensor; and

5 Fig. 15 is a cross-section view showing the related processes for fabricating a chip.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

10 The method for fabricating an array pH sensor and its readout circuit of the present invention are implemented by depositing a non-conductive pH sensing film onto an non-insulated substrate, thereby fabricating a separate array pH sensor and detecting the pH value of the solution by using such array pH sensor. In addition, the readout circuit of this array pH sensor, which includes pre-readout
15 circuit, a multiplexer, a rear end buffer circuit and an amplifier circuit, is fabricated according to the typical processes for making semiconductors. The array pH sensor and the readout circuit can be combined to be a hybrid array pH sensor. The array sensor is advantageous over the single sensing element, because larger sampling signals can decrease error resulting from the sensing
20 element and accuracy thereof is increased. When it is commercialized, the sensor would have high stability and accuracy.

The process for fabricating the array sensor of the present invention comprises the following steps:

Step1: providing a p-type silicon substrate with resistivity of 4~7 Ohm-cm
25 and silicon dioxide of 1000 angstrom;

Step 2: growing an Al film by using a metallic mask and a vacuum evaporation machine;

Step 3: growing a SnO₂ film by using a metallic mask and a sputter machine; and

5 Step 4: encapsulating the resulting product with epoxy resin.

The readout circuit portion is fabricated according to a 0.5 micrometer 2P2M n-well process provided by United Microelectronics Corp. (Hsinchu, TW), wherein the related processing conditions are shown in Fig. 14. The features for each layer of the sensor can be illustrated as follows:

- 10 1. The thickness of Cpoly is 0.2 micrometer (μm);
2. The thickness of Gpoly is 0.3 micrometer (μm);
3. The thickness of Metal1 is 0.6 micrometer (μm);
4. The thickness of Metal2 is 1.1 micrometer (μm);
5. The thickness of Passivation layer is 0.7 micrometer (μm);
- 15 6. The thickness of gate oxide layer is 135 angstrom (\AA); and
7. The total area of the chip is 1.8 mm².

Fig.1 is the cross-sectional view showing a sensing configuration of SnO₂/Al/SiO₂/Si. As can be seen in Fig. 1, such structure is easily fabricated according to the standard CMOS fabrication process, and can be a tin
20 dioxide/aluminum metal/silicon dioxide structure 1, which is constructed by depositing an aluminum layer 12 and a tin dioxide layer 13 onto a substrate 11, and encapsulating the resulting structure with epoxy resin 14 to form a opening channel. Via the aluminum layer 12, a conducting line 4 is led out.

Fig. 2 is the cross-sectional view showing the sensing configuration of
25 SnO₂/ITO/glass. Since the glass substrate is cost effective, the sensor with this

structure can be applied to fabricate disposable sensors. This structure is a tin dioxide/indium tin oxide/glass structure 2, which is constructed by depositing an indium tin oxide layer 22 and a tin dioxide layer 23 onto a glass substrate 21, and partially encapsulating the resulting structure with epoxy resin 24 to form a
5 opening channel. Via the indium tin oxide layer 22, a conducting line 4 is led out.

Please refer to Fig. 3. The flowchart for fabricating the array pH sensor of the present invention comprises the following steps:

Step 1: providing a silicon substrate 31, for example a p-type silicon
10 substrate with resistivity of 4~7 Ohm-cm and silicon dioxide layer of 1000 angstrom, wherein the silicon substrate can be replaced by glass substrates, ceramic substrates or polymeric substrates in order to broaden the applications of the sensor;

Step 2: growing an Al film 32 by using a metallic mask and a vacuum
15 evaporation machine;

Step 3: growing a SnO₂ film 33 by using a metallic mask and a sputter machine; and

Step 4: encapsulating the resulting product with epoxy resin 34.

The process for fabricating such sensor is easy because the procedures of
20 coating photoresist solutions and etching films are omitted.

Fig. 4 is a schematic view showing the Al layer mask, which is a metallic mask. The portions of the aluminum film to be deposited are indicated with the black portions. After the metallic mask is etched away, the Al film is deposited onto the metallic portions where the mask has been removed.

25 Fig. 5 is a schematic view showing the sensing membrane SnO₂ layer mask,

which is a metallic SnO₂ mask. The portions of the tin dioxide film to be deposited are indicated with the black portions. After the metallic mask is etched away, the tin dioxide film is deposited onto the metallic portions where the mask has been removed.

5 Fig. 6 is the configuration of the array pH sensor of the present invention. This array pH sensor comprises four sensing elements and four pre-amplifiers at the front end thereof. The respective sensing element is read by control circuits, and the pre-amplifier and the control circuits are compensated by the rear end amplifiers, thereby obtaining an output/input ratio of 1. The rear end readout
10 circuit of this array sensor can be used to receive different signals and amplifying these signals for determination. Thus, when the multiplexer is modified, a variety of array sensors can be fabricated for many applications such as fabrication of potentiometric sensor.

 Fig. 7 is the circuit configuration of the pre-amplifier for the array pH sensor.
15 The pre-amplifier is consisted of four CMOS devices so as to reduce the layout space.

 Fig. 8 shows the input/output ratio of the pre-amplifier. The output/input ratio is 0.7184 and an offset voltage is -1.097V. Accordingly, the signal would be decreased, when the sensing element is connected to the pre-amplifier.

20 Fig. 9 shows the circuit configuration of the switch of the control portion, which is consisted of an inverter and a CMOS switch.

 Fig. 10 shows the circuit configuration of a 2 to 4 decoder of the control portion, which is consisted of six inverters and four NAND circuits.

 Fig. 11 is a schematic diagram showing the output/input ratio of the circuit
25 combined the pre-amplifier and the control circuit. The output/input ratio is

0.675 and the offset voltage is -1.095V. Accordingly, the signal would be further decreased, when the sensing element was connected to the pre-amplifier and multiplexer.

Fig. 12 is a schematic diagram showing the output/input ratio of the circuit of the array pH sensor. As can be seen in Fig. 12, due to the amplification of the rear end readout circuit, the signals of the sensing membrane can be compensated to the initial values and the ratio of the output voltage to the input voltage is 1.04.

It was in order to compensate the decreasing of pre-circuit. So, The input output ratio is 1.04 of the array pH sensor system, when the circuit included the pre-amplifier, multiplexer, buffer and post amplifier.

Fig. 13 is a schematic diagram showing the readout signal of the array pH sensor. As can be seen in Fig. 13, four sets of signals are stable, indicating a stable fabrication process of this array sensor.

Fig. 14 is a schematic correction curve of the readout signal of the array pH sensor. The correction curve shows a linear pH sensitivity of 0.99969, which indicates an excellent performance of the array ion sensor.

Fig. 15 is a cross-section view showing the related processes for fabricating a chip. In Fig. 15, the relative positions of the layer structures of a 0.5 micrometer n-well double polysilicon double-metal process are shown.

Many changes and modifications in the above described embodiment of the invention can, of course, be carried out without departing from the scope thereof. Accordingly, to promote the progress in science and the useful arts, the invention is disclosed and is intended to be limited only by the scope of the appended claims.

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